

(19)

Europäisches Patentamt
European Patent Office
Office européen des brevets



(11)

EP 1 359 168 A1

(12)

EUROPEAN PATENT APPLICATION

(43) Date of publication:
05.11.2003 Bulletin 2003/45

(51) Int Cl.7: **C08F 10/02, C08F 2/00**

(21) Application number: **02358009.5**

(22) Date of filing: **03.05.2002**

(84) Designated Contracting States:
AT BE CH CY DE DK ES FI FR GB GR IE IT LI LU
MC NL PT SE TR
 Designated Extension States:
AL LT LV MK RO SI

(72) Inventor: **The designation of the inventor has not yet been filed**

(74) Representative: **De Kezel, Eric et al**
BP Lavéra S.N.C.,
LPID/CRT,
BP N 6
13117 Lavéra (FR)

(71) Applicant: **BP Lavéra SNC**
95866 Cergy Pontoise Cedex (FR)

(54) **Rotomoulding polyethylene and method for producing same**

(57) The present invention relates to a method for producing rotomoulding polyethylene by fluidised bed gas phase polymerisation of ethylene. The present invention further relates to the improved rotomoulding polyethylene obtainable by the invention process.

EP 1 359 168 A1

Description

[0001] The present invention relates to a method for producing rotomoulding polyethylene by fluidised bed gas phase polymerisation of ethylene. The present invention further relates to the improved rotomoulding polyethylene obtainable by the invention process.

[0002] Processes for the co-polymerisation of olefins in the gas phase are well known in the art. Such processes can be conducted for example by introducing the gaseous monomer and comonomer into a stirred and/or gas fluidised bed comprising polyolefin and a catalyst for the polymerisation.

[0003] In the gas fluidised bed polymerisation of olefins, the polymerisation is conducted in a fluidised bed reactor wherein a bed of polymer particles is maintained in a fluidised state by means of an ascending gas stream comprising the gaseous reaction monomer. The start-up of such a polymerisation generally employs a bed of polymer particles similar to the polymer, which it is desired to manufacture. During the course of polymerisation, fresh polymer is generated by the catalytic polymerisation of the monomer, and polymer product is withdrawn to maintain the bed at more or less constant volume. An industrially favoured process employs a fluidisation grid to distribute the fluidising gas to the bed, and to act as a support for the bed when the supply of gas is cut off. The polymer produced is generally withdrawn from the reactor via a discharge conduit arranged in the lower portion of the reactor, near the fluidisation grid. The fluidised bed consists in a bed of growing polymer particles. This bed is maintained in a fluidised condition by the continuous upward flow from the base of the reactor of a fluidising gas.

[0004] The polymerisation of olefins is an exothermic reaction and it is therefore necessary to provide means to cool the bed to remove the heat of polymerisation. In the absence of such cooling the bed would increase in temperature and, for example, the catalyst becomes inactive or the bed commences to fuse. In the fluidised bed polymerisation of olefins, the preferred method for removing the heat of polymerisation is by supplying to the polymerisation reactor a gas, the fluidising gas, which is at a temperature lower than the desired polymerisation temperature, passing the gas through the fluidised bed to conduct away the heat of polymerisation, removing the gas from the reactor and cooling it by passage through an external heat exchanger, and recycling it to the bed. The temperature of the recycle gas can be adjusted in the heat exchanger to maintain the fluidised bed at the desired polymerisation temperature. In this method of polymerising alpha olefins, the recycle gas generally comprises the monomer and comonomer olefins, optionally together with, for example, an inert diluent gas such as nitrogen or a gaseous chain transfer agent such as hydrogen. Thus, the recycle gas serves to supply the monomer to the bed, to fluidise the bed, and to maintain the bed at the desired temperature.

Monomers consumed by the polymerisation reaction are normally replaced by adding make up gas or liquid to the polymerisation zone or reaction loop.

[0005] A gas fluidised bed polymerisation reactor is typically controlled to achieve a desired melt index and density for the polymer at an optimum production. Conditions within the polymerisation reactor have to be carefully controlled to reduce the risk of agglomerate and/or sheet formation which may ultimately lead to bed instabilities and a need to terminate the reaction and shut down the reactor. This is the reason why commercial scale reactors are designed to operate well within proven stable operating zones and why the reactors are used in a carefully circumscribed fashion.

[0006] It has now been found a new process for producing rotomoulding polyethylene in fluidised bed gas phase reactor, wherein an improved process-operating envelope is used. Thus, the present invention relates to a process for producing rotomoulding polyethylene, having a density A comprised between 930 and 944 kg/m³ and a melt index B comprised between 3 and 7.8, by (co-)polymerisation of ethylene in a fluidised bed gas phase reactor, said process comprising

determining the instantaneous density d and melt index MI of the polyethylene powder exiting the reactor, allowing the density and melt index to vary around their A and B values by a value of plus or minus 3 kg/m³ for the density and plus or minus 30% for the melt index,

characterised in that the operating temperature is controlled such that

1. the RTSE factor is first maintained in the operating-envelope corresponding to the d and MI values of the polyethylene produced, and
2. the RTSE factor is maintained between 4.2 and 4.4.

[0007] The present invention further relates to a rotomoulding polyethylene grade having a density comprised between 930 and 944 kg/m³ and a melt index comprised between 3 and 7.8 characterised in an ESCR property equal or higher than 400 h and a Charpy property equal or higher than 10kJ/m².

[0008] The ESCR can be measured according to ASTM-D-1693.

[0009] The Charpy can be measured according to ISO 179-2. Preferably, the Charpy value is equal or higher than 14kJ/m².

[0010] The densities can be measured according to ASTM-D-792 and defined as in ASTM-D-1248-84. The rotomoulding polyethylene of the present invention has a density comprised between 930 and 944, preferably between 933 and 941 kg/m³.

[0011] The melt index can be measured according to ASTM-D-1238, condition A (2.16kg). The rotomoulding polyethylene of the present invention has a melt index comprised between 3 and 7.8, preferably between 3 and

7 g/10min.

[0012] According to the present invention, the density and melt index are respectively allowed to vary around their A and B values by a value of plus or minus 3 kg/m³ for the density and plus or minus 30% for the melt index. It means, for example, that for a rotomoulding polyethylene with A=937 and B=5, acceptable variations are for density from 934 to 941 and for melt index from 3.5 to 6.5. According to a preferred embodiment of the present invention, the density and melt index are respectively allowed to vary around their A and B values by a value of plus or minus 2 kg/m³ for the density and plus or minus 15% for the melt index.

[0013] The RTSE factor is indicated in the attached tables (figure 1 to 20). A RTSE value comprised between 4.2 and 4.4 corresponds to each density/melt index couple. To every RTSE corresponds an operating temperature. For density or melt index values that are falling at the border of operating envelopes (window), the corresponding operating temperature envelope can easily be calculated by making linear interpolations. For example, in figure 1, for a 932 / 3.7 density /melt index couple, the operating temperature at an RTSE of 4.3 is the average between 96.2°C (i.e. operating temperature for a 932 / 3.8 density /melt index couple at RTSE of 4.3) and 96.6°C (i.e. operating temperature for a 932 / 3.6 density /melt index couple at RTSE of 4.3), i.e. 96.4°C.

[0014] As already indicated, the invention is characterised in that the operating temperature is controlled such that the RTSE factor is first maintained in the operating-envelope corresponding to the D and MI values of the polyethylene produced, and the RTSE factor is maintained between 4.2 and 4.4.

According to a preferred embodiment of the present invention, during the production of a specific rotomoulding polyethylene grade, the RTSE factor is allowed to vary only by plus or minus 0.07, preferably 0.05 across the operating envelopes, said variation occurring within a minimum of 4 hours of operation, preferably within a minimum of 8 hours of operation.

[0015] This process is preferably applied during the fluidised bed gas phase polymerisation of olefins, and may also advantageously be used during start-up and especially during product grade transition between two rotomoulding polyethylene.

[0016] The instantaneous density and melt index properties correspond to the properties of the resin formed instantaneously in the reacting conditions at a given time. The "instantaneous properties" are different from the pellet properties which correspond to a mixture of different resins formed continuously in the fluidised bed (averaging effect).

[0017] The process according to the present invention is particularly suitable for the manufacture of copolymers of ethylene. Preferred alpha-olefins used in combination with ethylene in the process of the present invention are those having from 4 to 8 carbon atoms. The

preferred alpha-olefins are but-1-ene, pent-1-ene, hex-1-ene, 4-methylpent-1-ene, oct-1-ene and butadiene, the most preferred comonomer being the hex-1-ene.

[0018] When liquid condenses out of the recycle gaseous stream, it can be a condensable monomer, e.g. but-1-ene, hex-1-ene, 4-methylpent-1-ene or octene used as a comonomer, and/or an optional inert condensable liquid, e.g. inert hydrocarbon(s), such as C₄-C₈ alkane(s) or cycloalkane(s), particularly butane, pentane or hexane.

The process is particularly suitable for polymerising olefins at an absolute pressure of between 0.5 and 6 MPa and at a temperature of between 90°C and 110°C.

[0019] The polymerisation is preferably carried out continuously in a vertical fluidised bed reactor according to techniques known in themselves and in equipment such as that described in European patent application EP-0 855 411, French Patent No. 2,207,145 or French Patent No. 2,335,526. The process of the invention is particularly well suited to industrial-scale reactors of very large size.

[0020] The polymerisation reaction may be carried out in the presence of a catalyst system of the Ziegler-Natta type, consisting of a solid catalyst essentially comprising a compound of a transition metal and of a cocatalyst comprising an organic compound of a metal (i.e. an organometallic compound, for example an alkylaluminium compound). High-activity catalyst systems have already been known for a number of years and are capable of producing large quantities of polymer in a relatively short time, and thus make it possible to avoid a step of removing catalyst residues from the polymer. These high-activity catalyst systems generally comprise a solid catalyst consisting essentially of atoms of transition metal, of magnesium and of halogen. The process is also suitable for use with Ziegler catalysts supported on silica. The process is also especially suitable for use with metallocene catalysts in view of the particular affinity and reactivity experienced with comonomers and hydrogen. The process can also be advantageously applied with a late transition metal catalyst, i.e. a metal from Groups VIIIb or Ib (Groups 8-11) of the Periodic Table. In particular the metals Fe, Co, Ni, Ru, Rh, Pd, Os, Ir, and Pt are preferred, especially Fe, Co and Ni. The late transition metal complex may comprise bidentate or tridentate ligands, preferably coordinated to the metal through nitrogen atoms. As examples are those complexes disclosed in WO96/23010. Suitable iron and/or cobalt complexes catalysts can also be found in WO98/27124 or in WO99/12981.

It is also possible to use a high-activity catalyst consisting essentially of a chromium oxide activated by a heat treatment and associated with a granular support based on a refractory oxide.

The catalyst may suitably be employed in the form of a prepolymer powder prepared beforehand during a prepolymerisation stage with the aid of a catalyst as described above. The prepolymerisation may be carried

out by any suitable process, for example, polymerisation in a liquid hydrocarbon diluent or in the gas phase using a batch process, a semi-continuous process or a continuous process.

Claims

1. Process for producing rotomoulding polyethylene, having a density A comprised between 930 and 944 kg/m³ and a melt index B comprised between 3 and 7.8, by (co-)polymerisation of ethylene in a fluidised bed gas phase reactor, said process comprising determining the instantaneous density d and melt index MI of the polyethylene powder exiting the reactor, allowing the density and melt index to vary around their A and B values by a value of plus or minus 3 kg/m³ for the density and plus or minus 30% for the melt index, **characterised in that** the operating temperature is controlled such that the RTSE factor is first maintained in the operating-envelope corresponding to the d and MI values of the polyethylene produced, and the RTSE factor is maintained between 4.2 and 4.4.
2. Process according to claim 1 wherein the density and melt index are respectively allowed to vary around their A and B values by a value of plus or minus 3 kg/m³ for the density and plus or minus 30% for the melt index.
3. Process according to claim 2 wherein the density and melt index are respectively allowed to vary around their A and B values by a value of plus or minus 2 kg/m³ for the density and plus or minus 15% for the melt index.
4. Process according to any of the preceding claims wherein the RTSE factor is allowed to vary only by plus or minus 0.07 across the operating envelope (s), said variation occurring within a minimum of 4 hours of operation.
5. Process according to claim 4 wherein the RTSE variation is only allowed within a minimum of 8 hours of operation.
6. Process according to claims 4 and 5 wherein the RTSE factor is allowed to vary only by plus or minus 0.05 across the operating envelope(s).
7. Process according to any of the preceding claims wherein it applied during product grade transition between two rotomoulding polyethylene.
8. Process according to any of the preceding claims wherein the polyethylene is a copolymer of ethylene and hex-1-ene.
9. Process according to any of the preceding claims wherein the rotomoulding polyethylene has a density comprised between 933 and 941 kg/m³ and a melt index comprised between 3 and 7 g/10min.
10. Rotomoulding polyethylene grade obtainable by any of the preceding claims and having a density comprised between 930 and 944 kg/m³ and a melt index comprised between 3 and 7.8 **characterised in** an ESCR property equal or higher than 400 h and a Charpy property equal or higher than 10kJ/m².

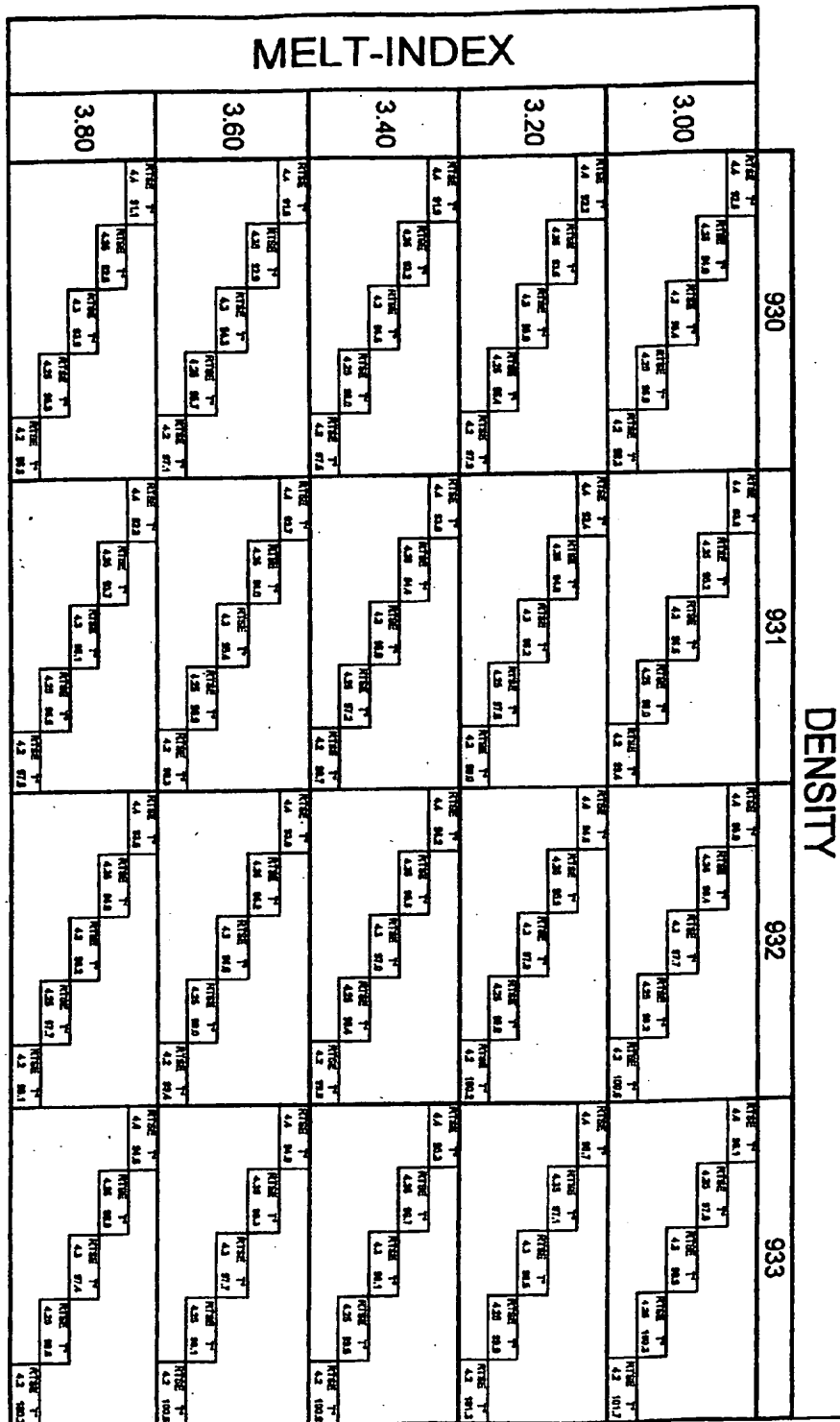


Figure 1

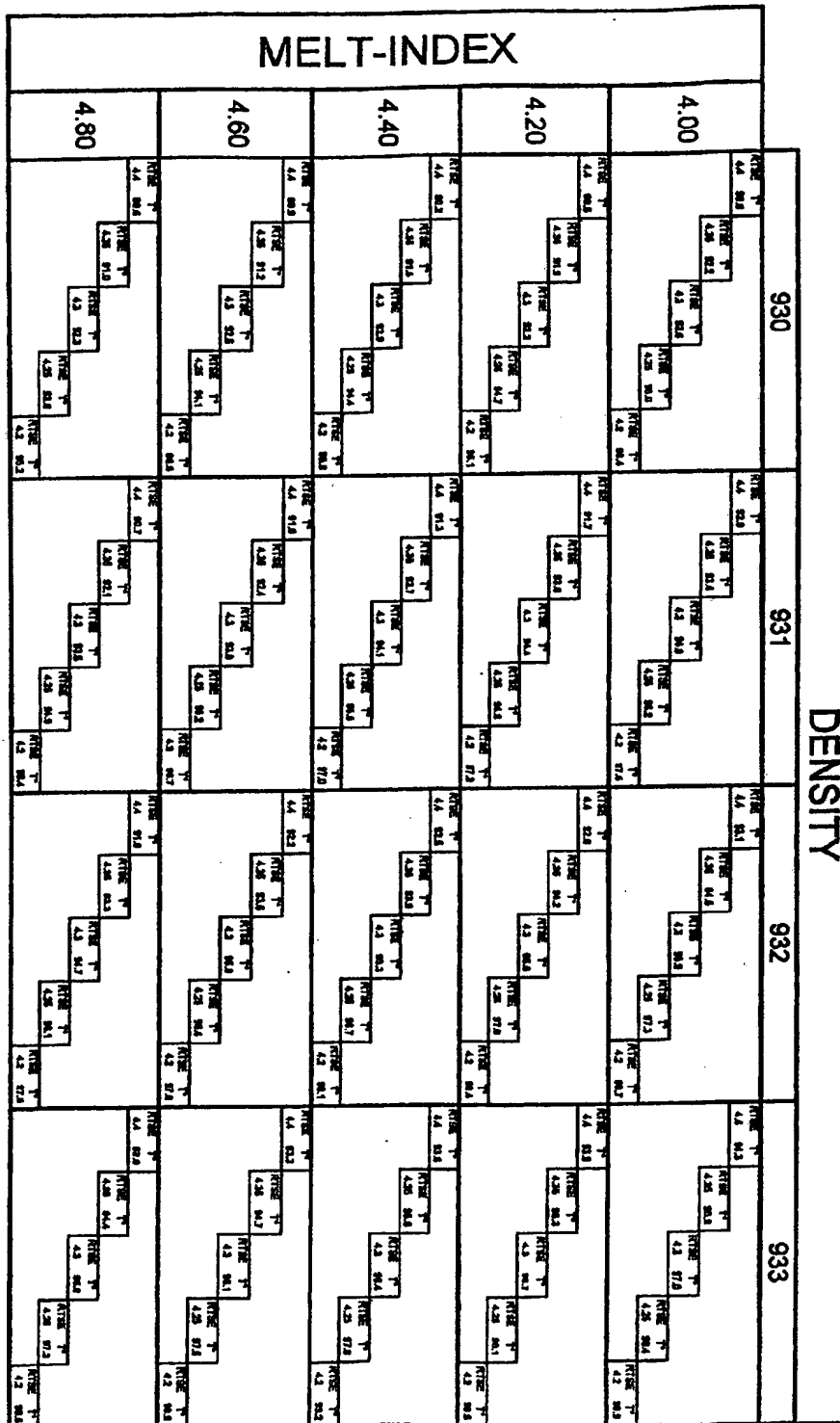


Figure 2

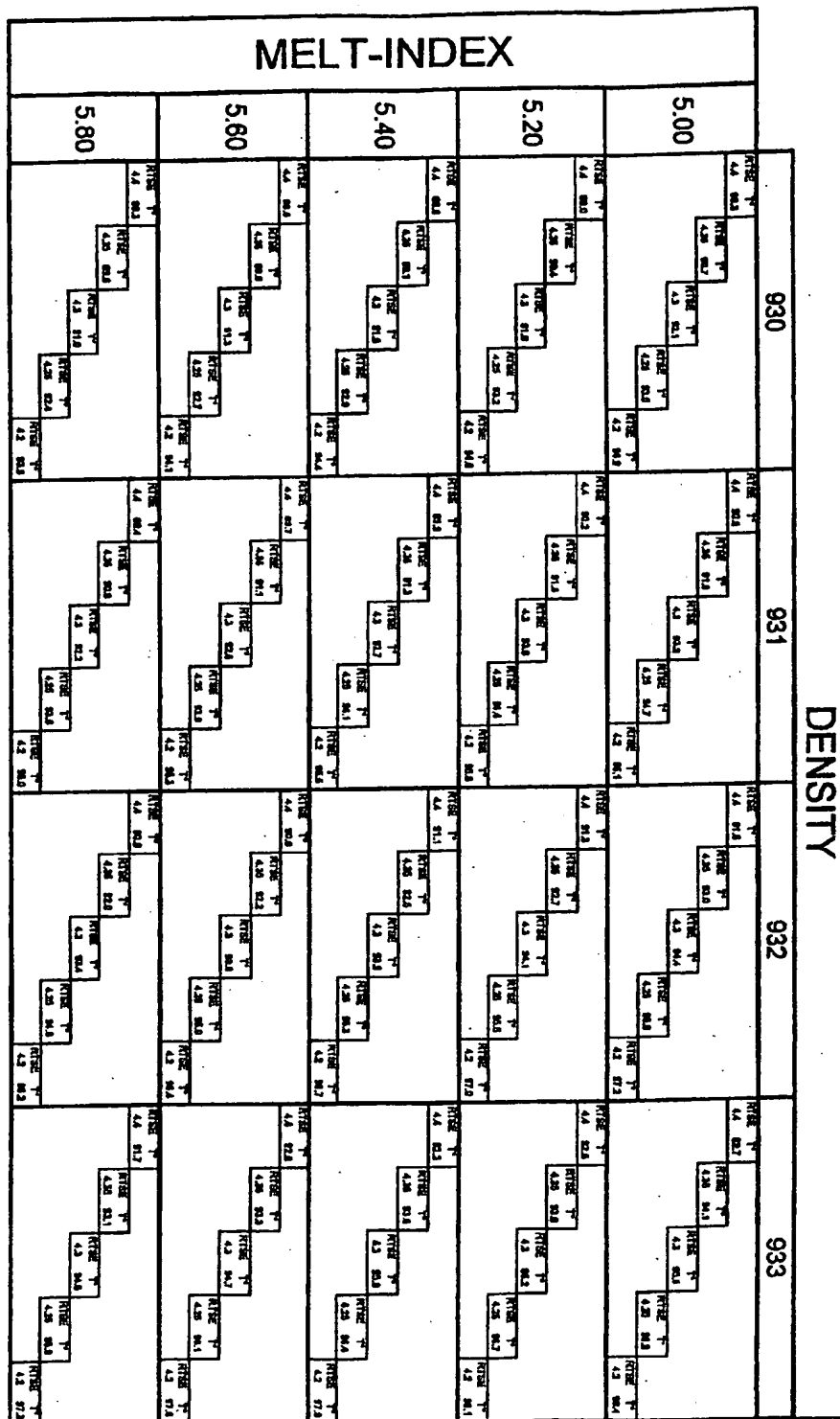


Figure 3

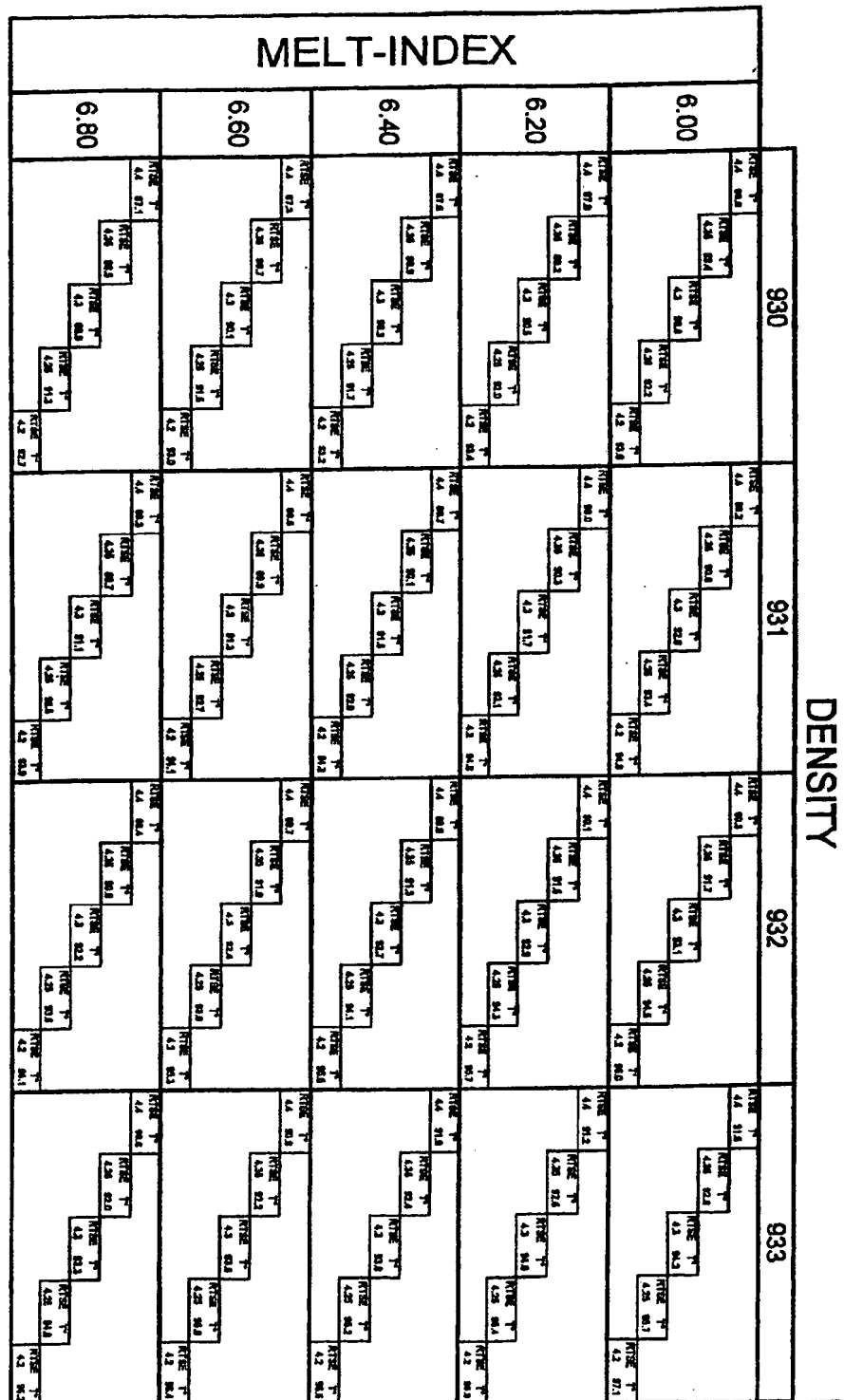
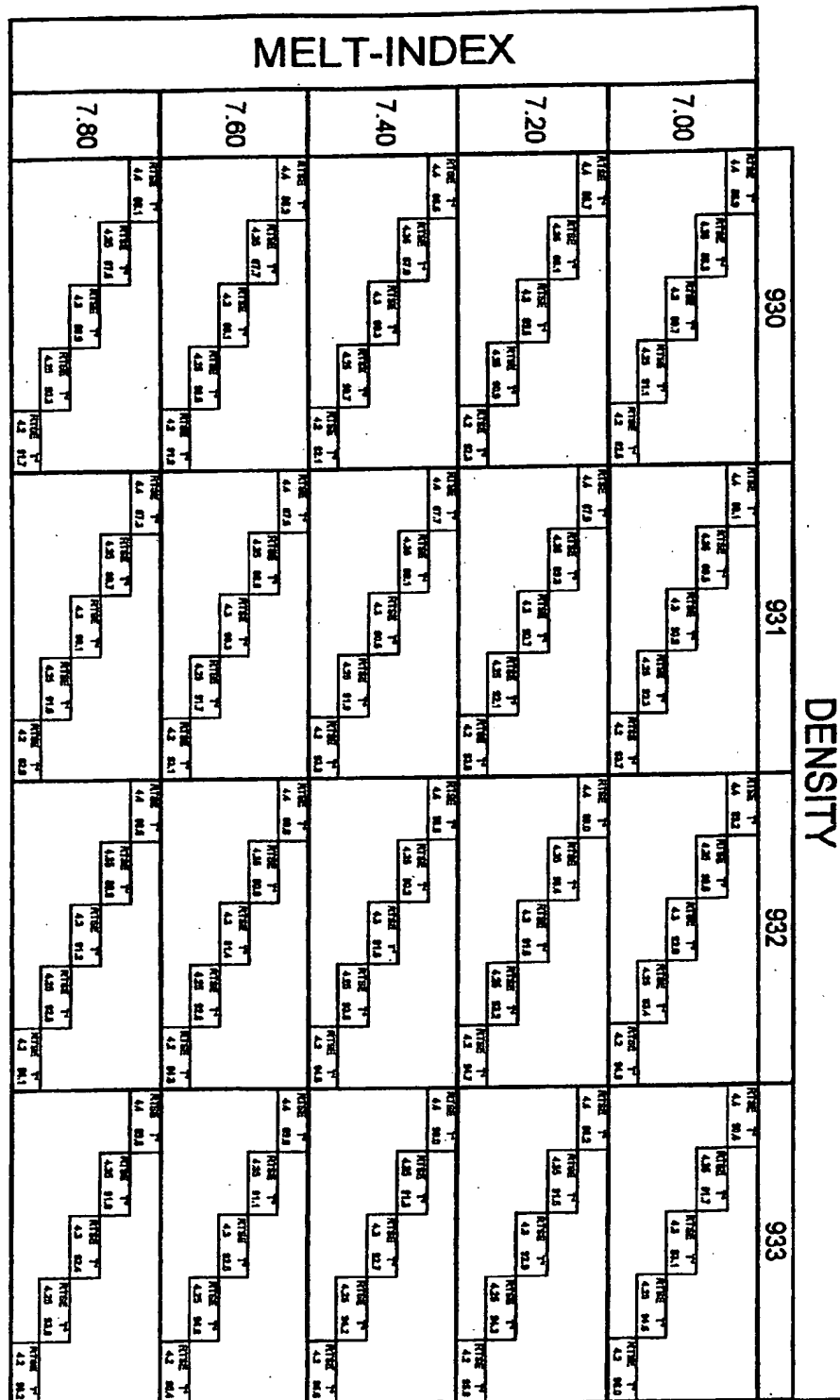


Figure 4



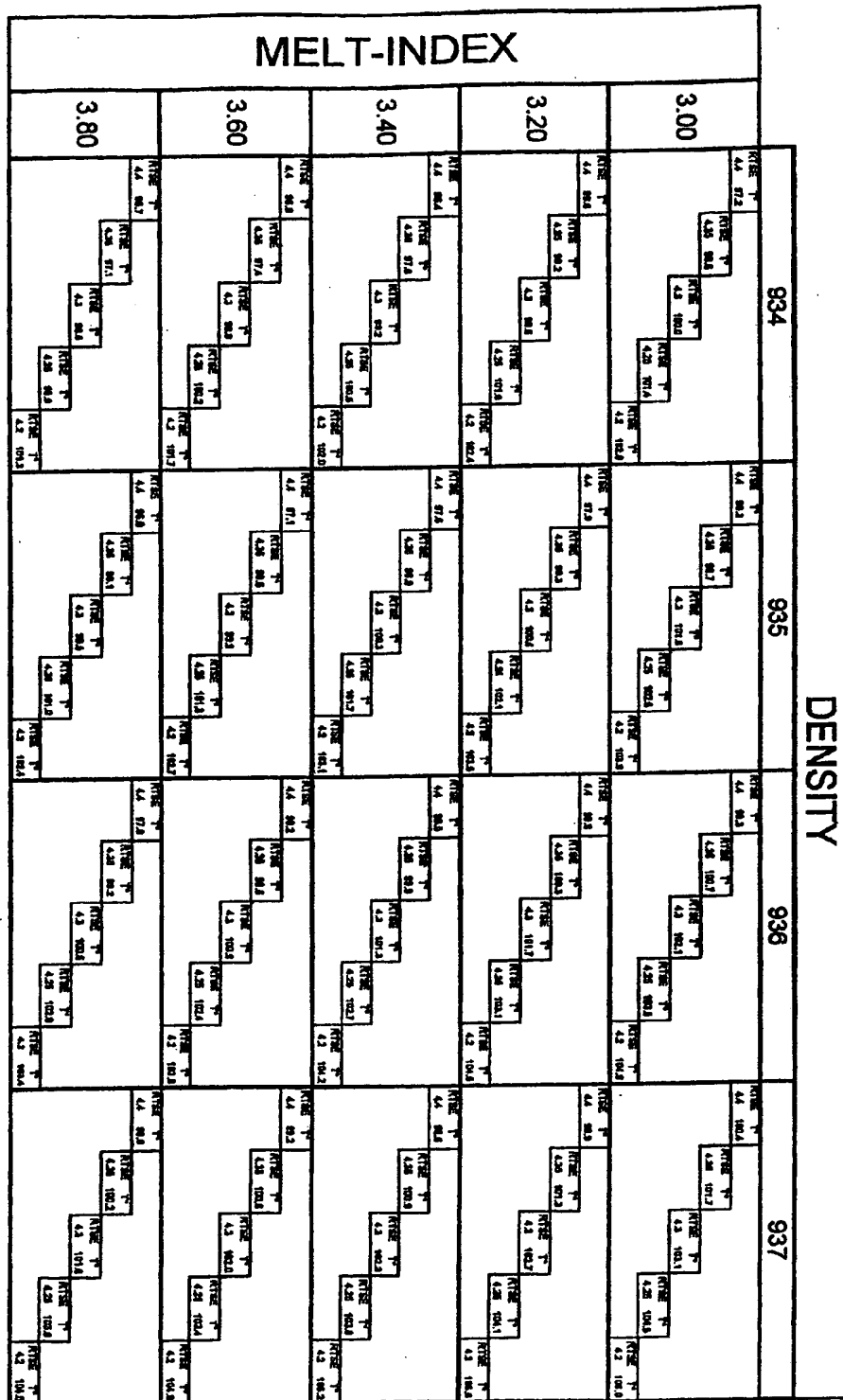
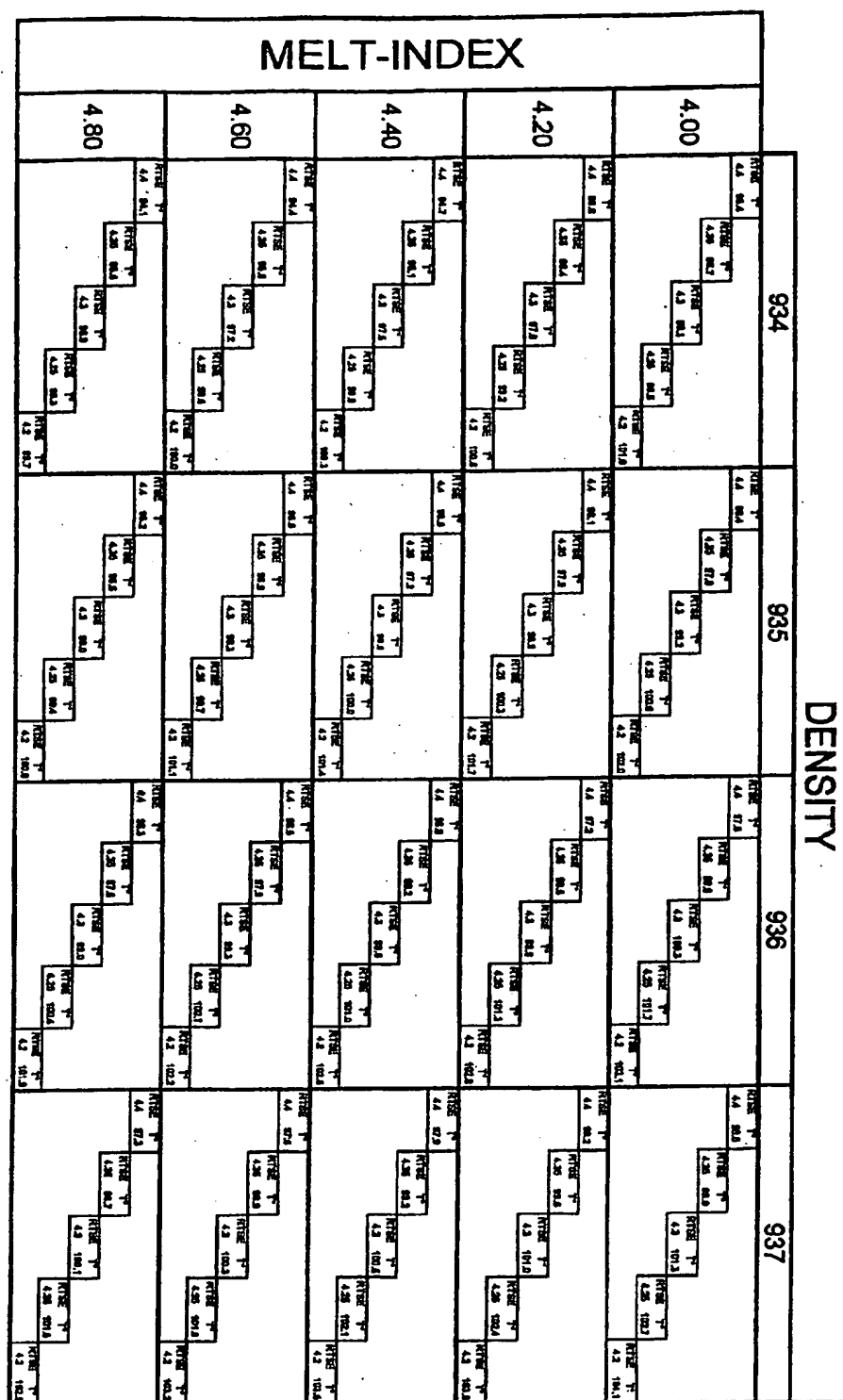


Figure 6



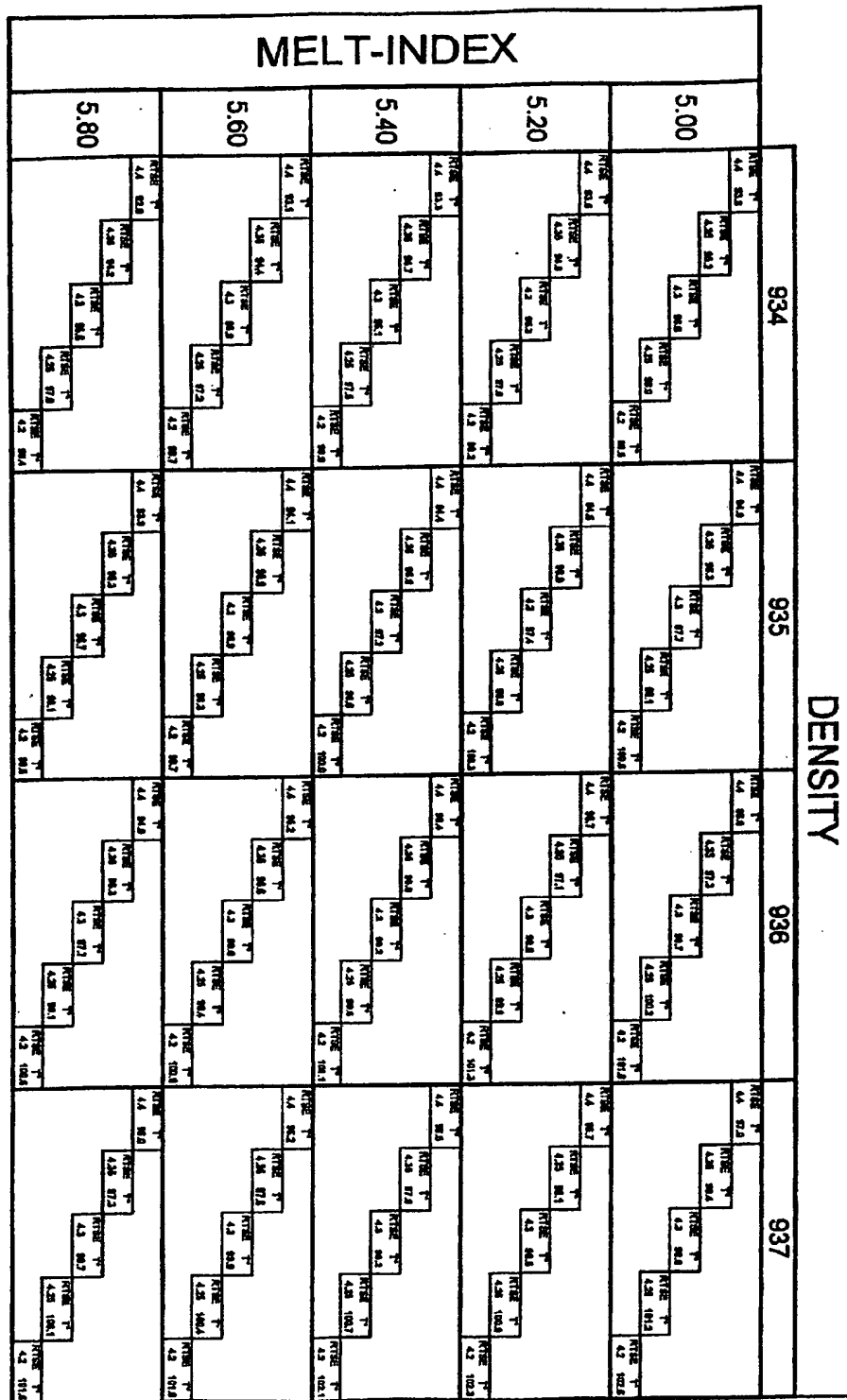


Figure 8

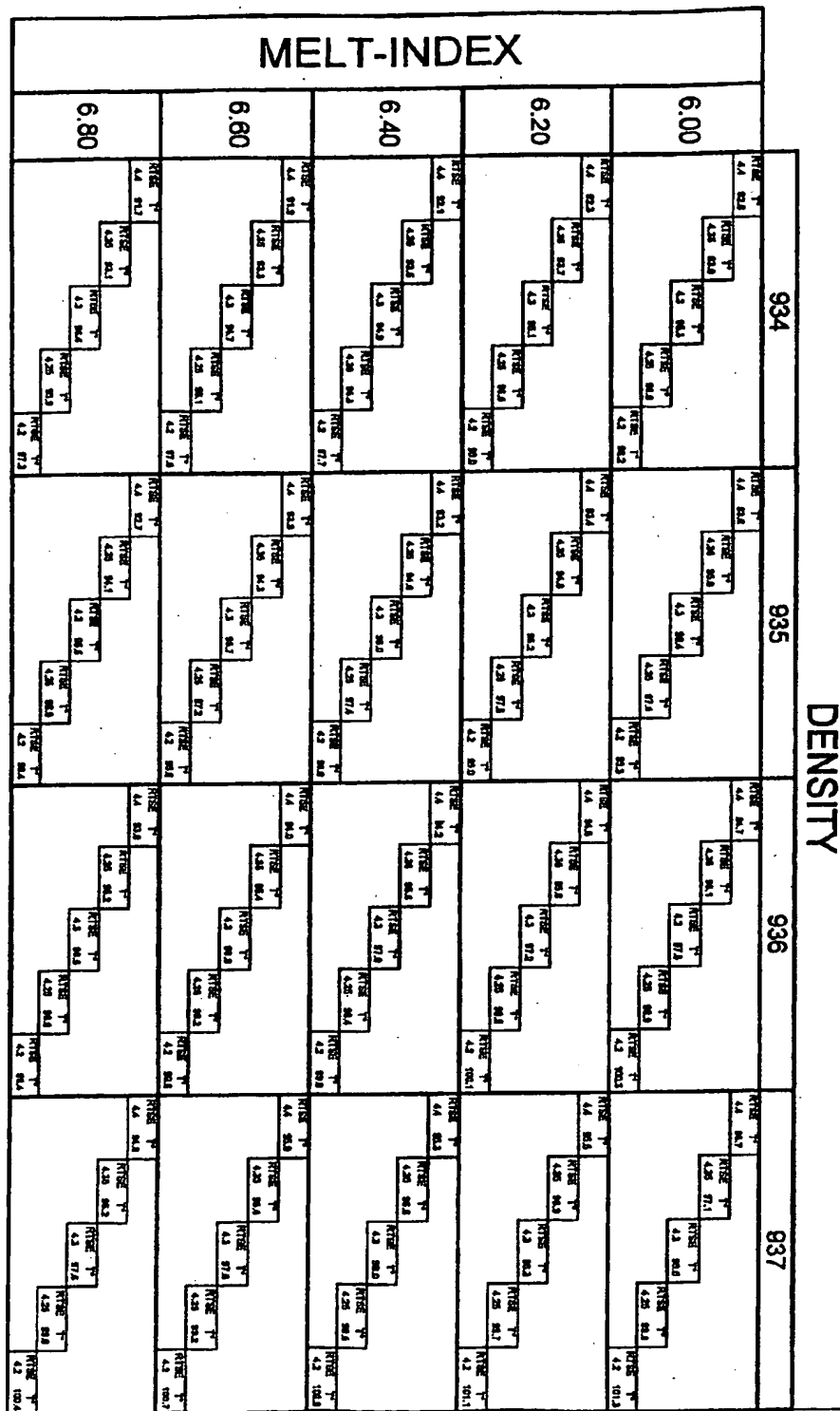


Figure 9

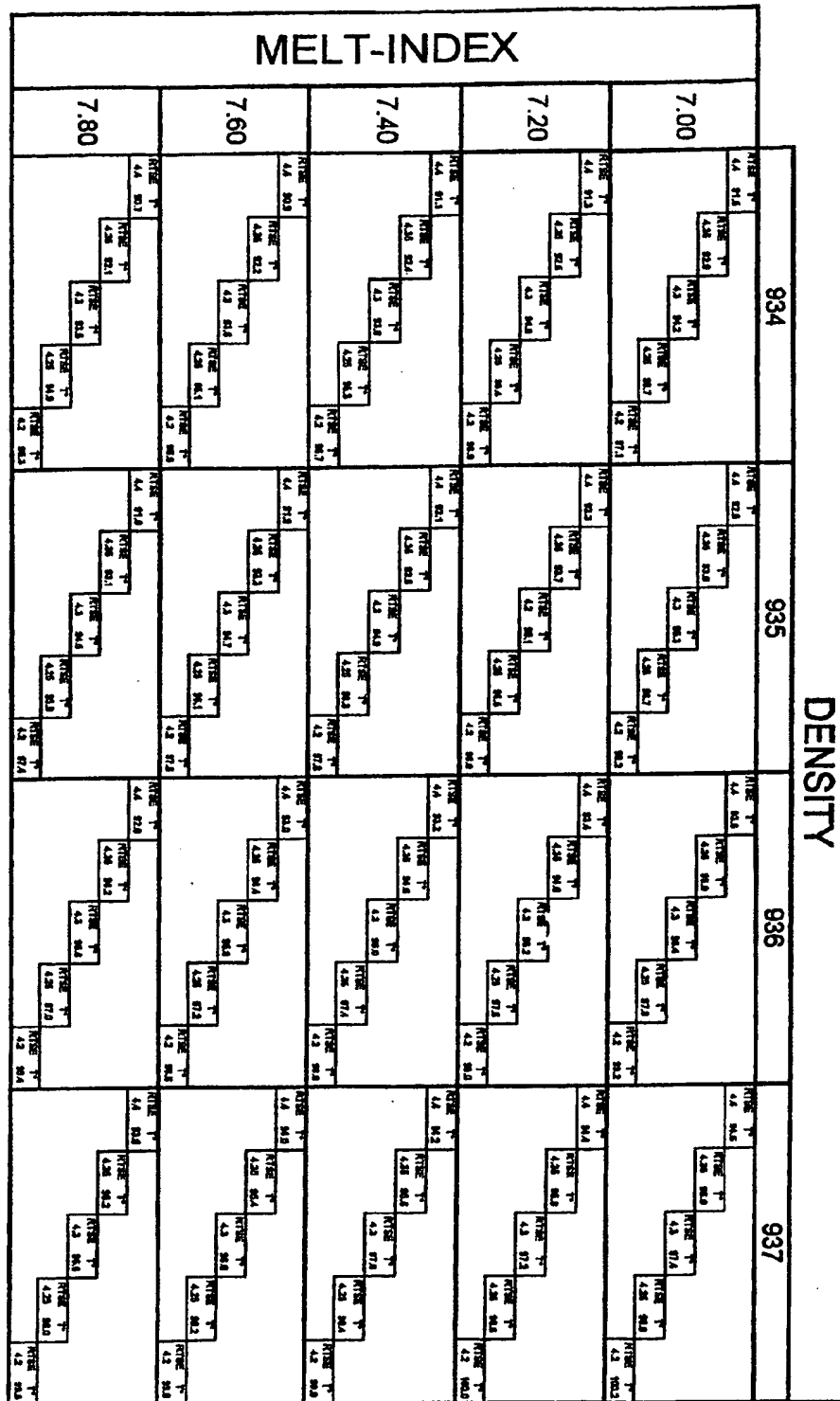


Figure 10

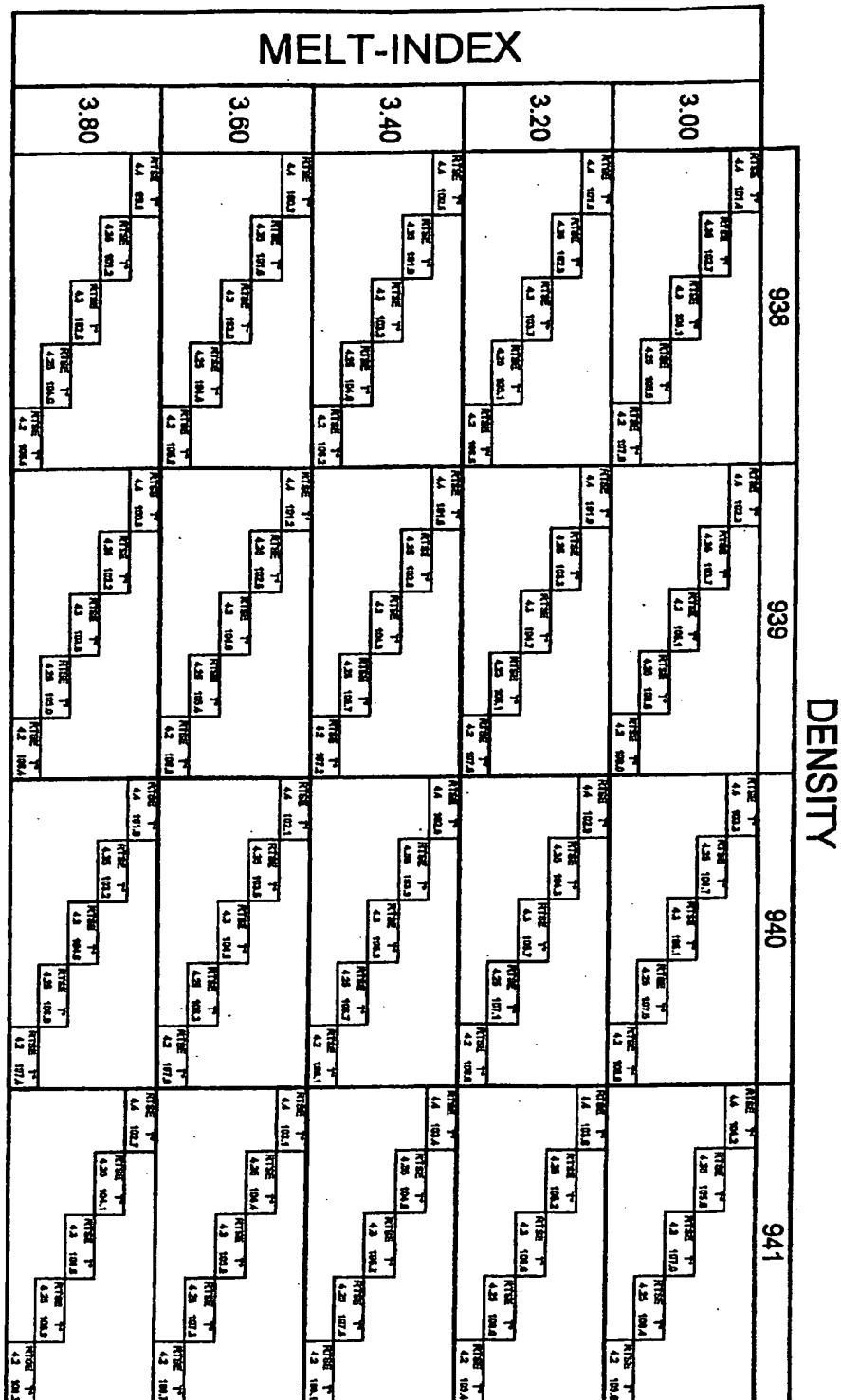
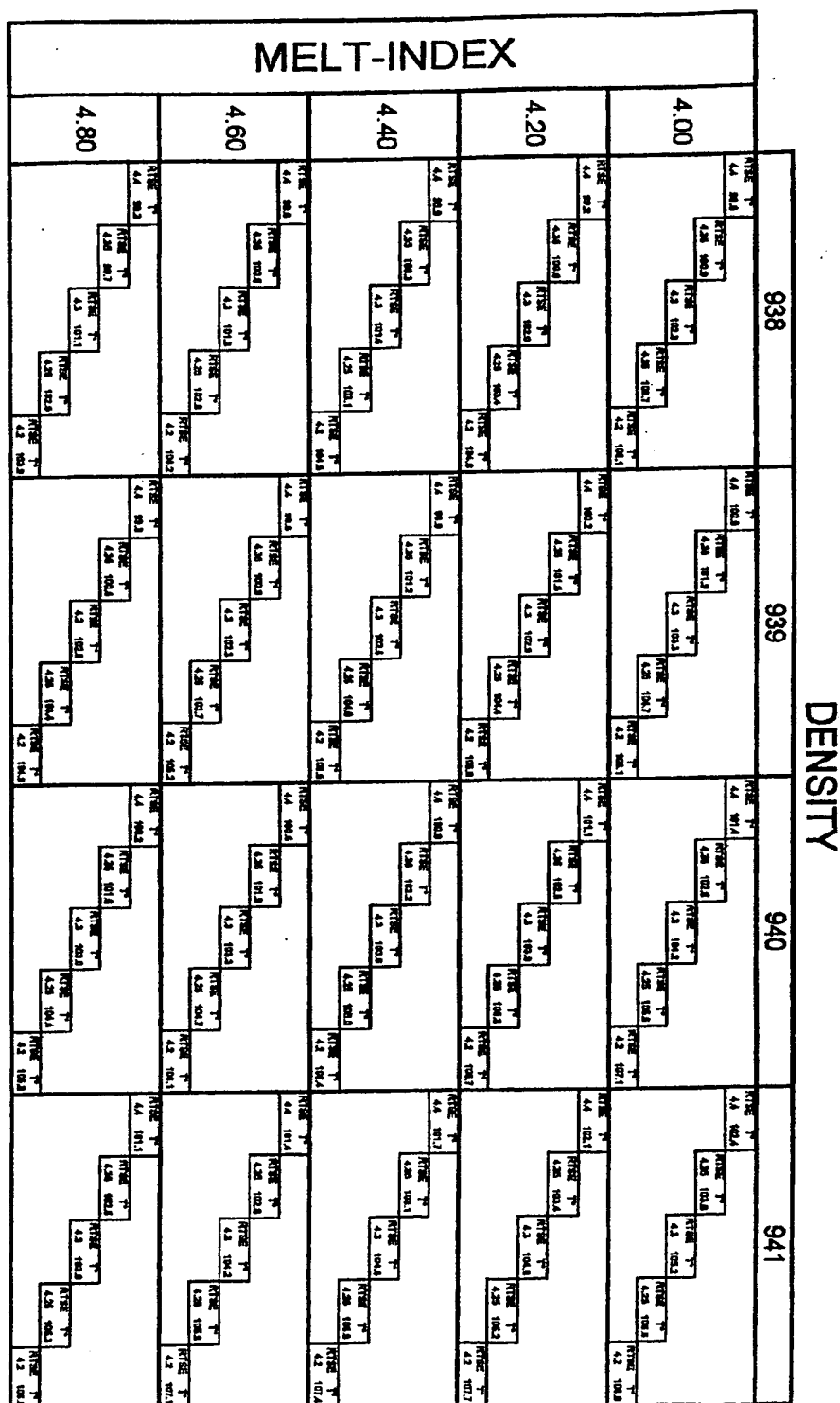


Figure 11



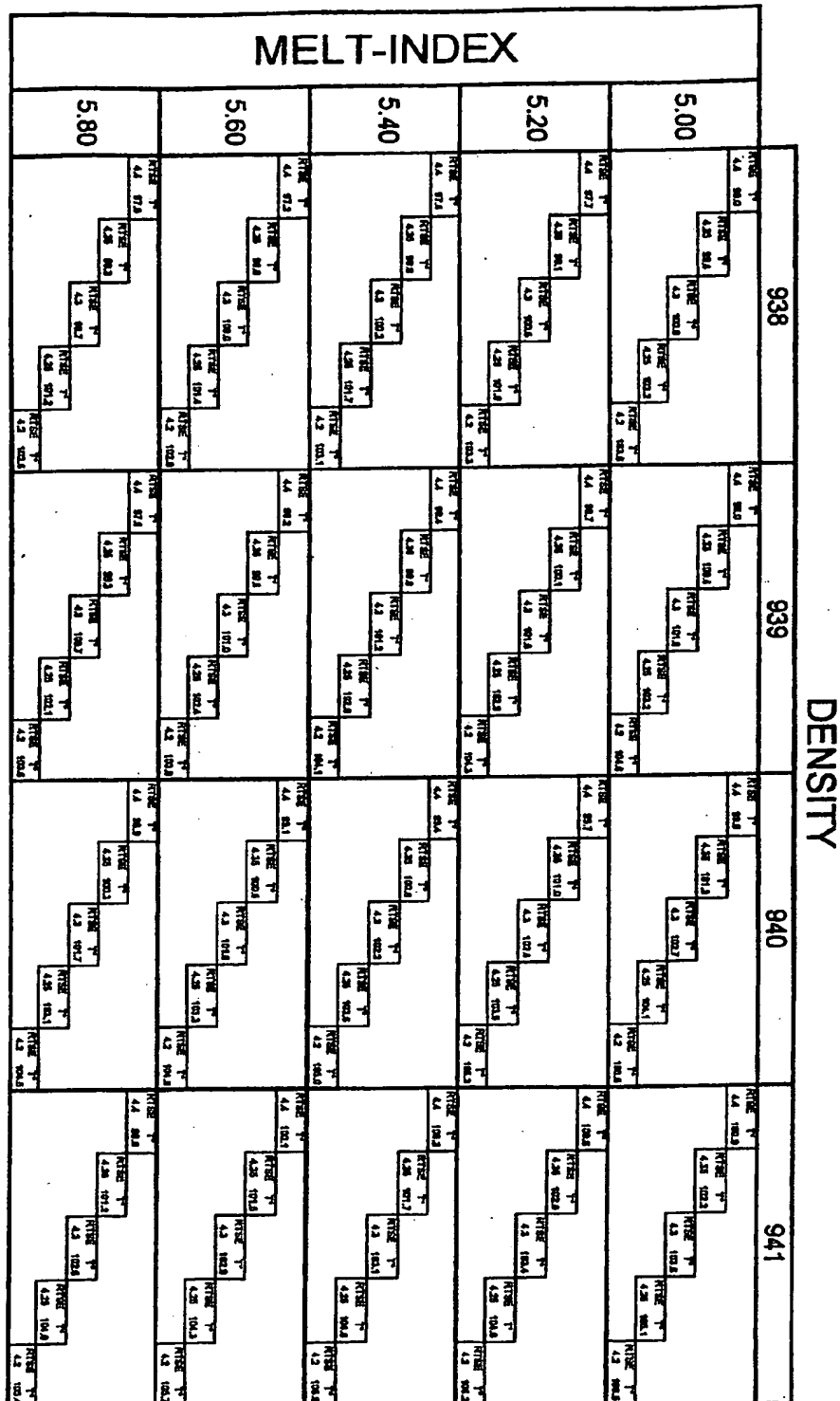


Figure 13

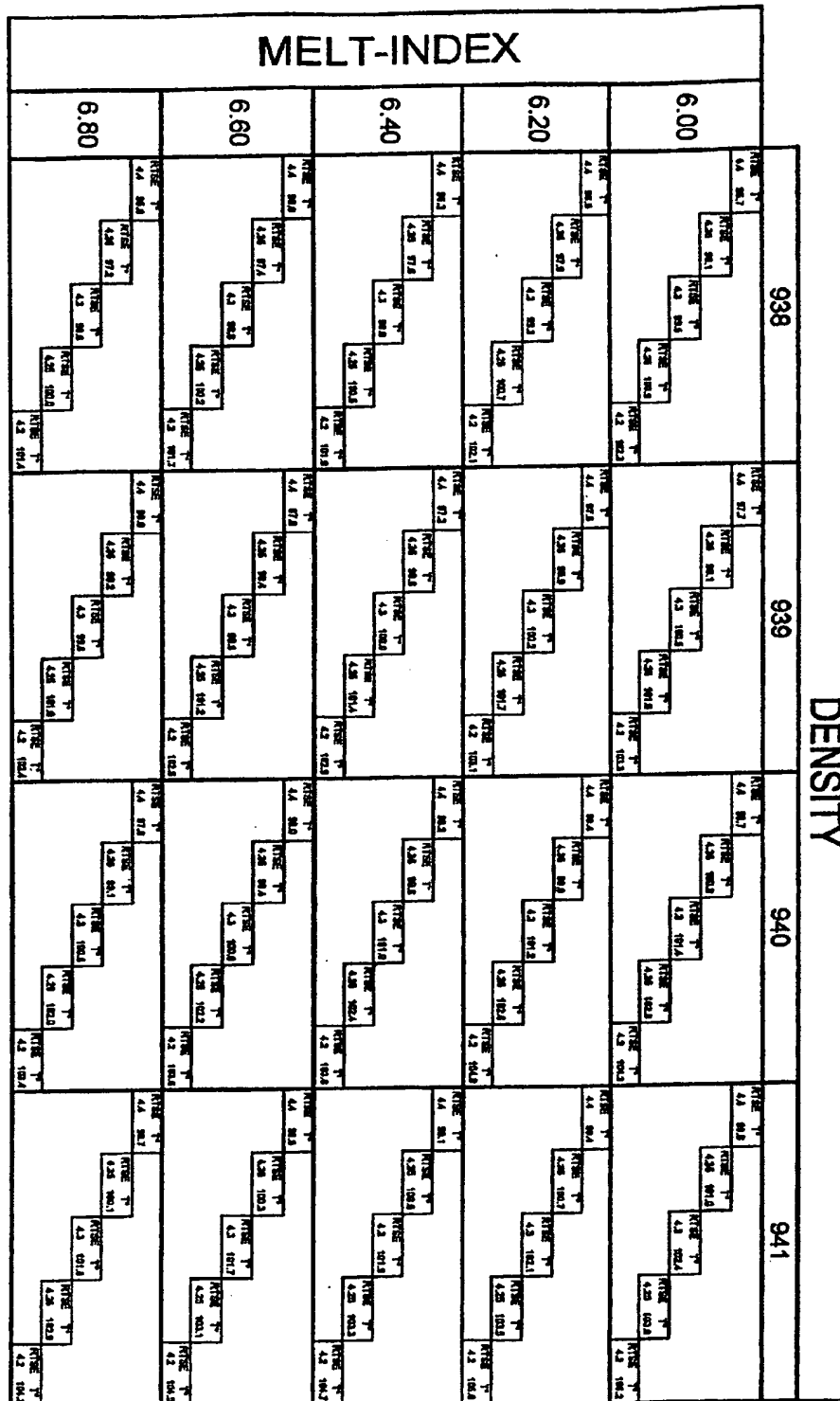


Figure 14

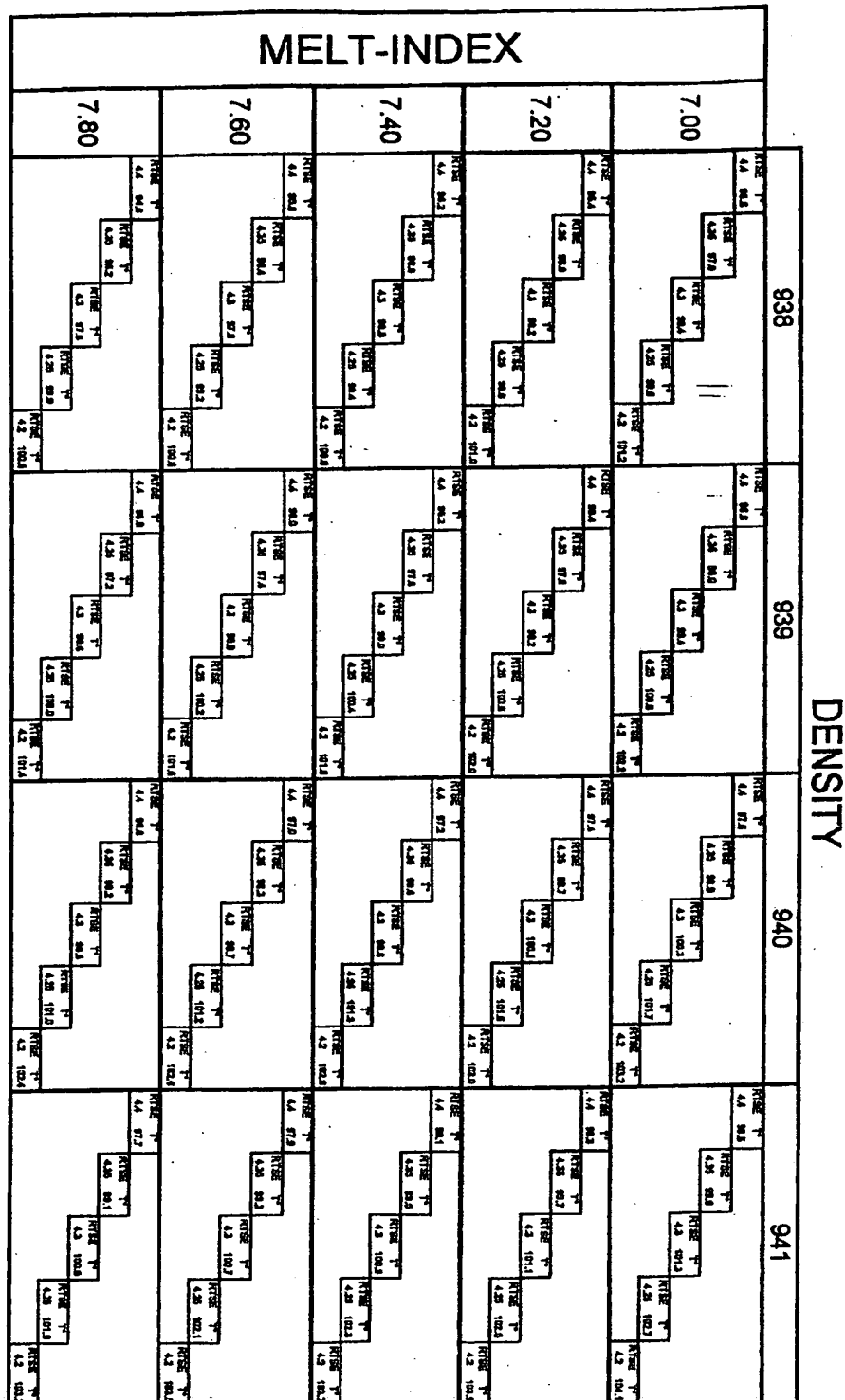


Figure 15.

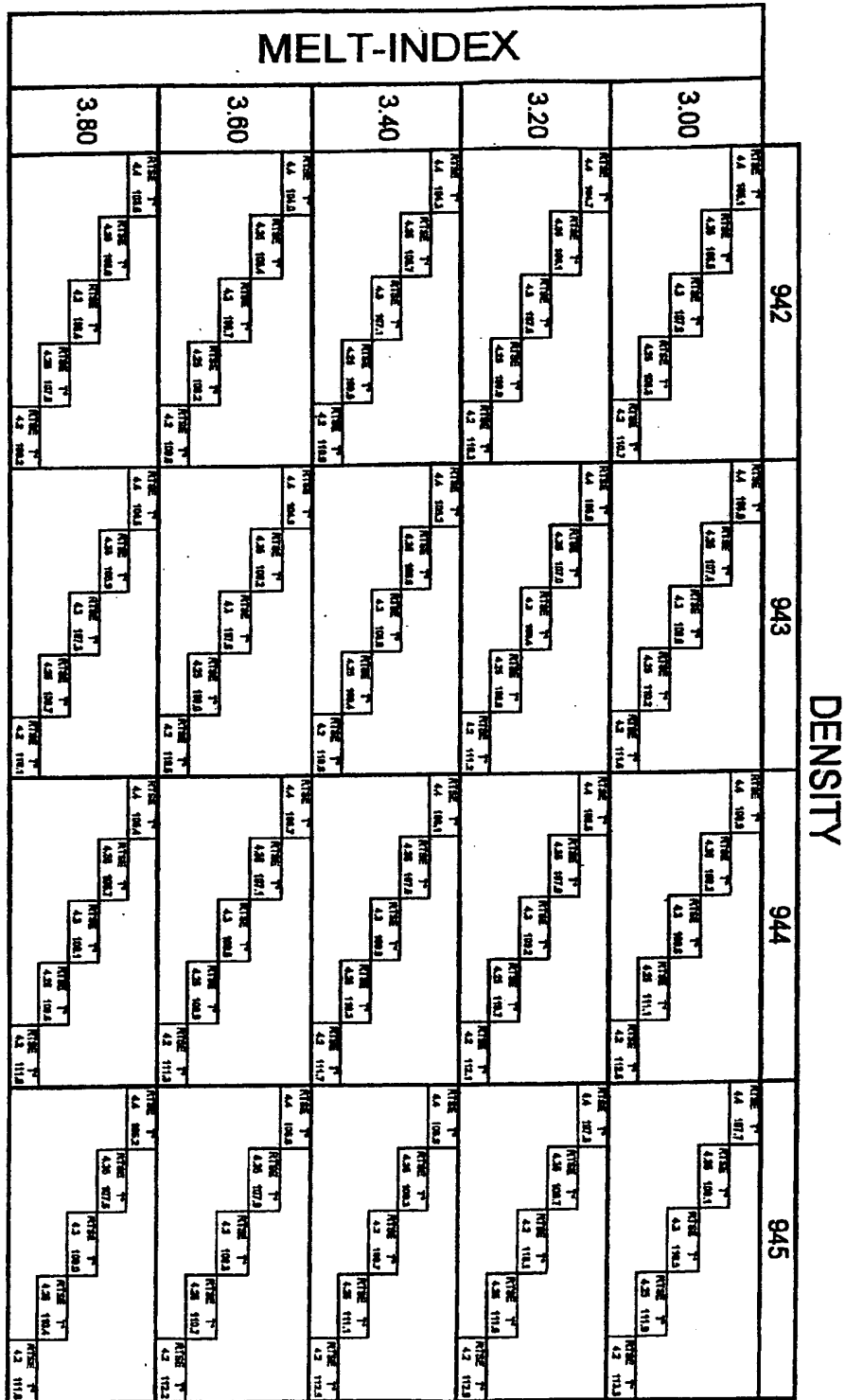


Figure 16

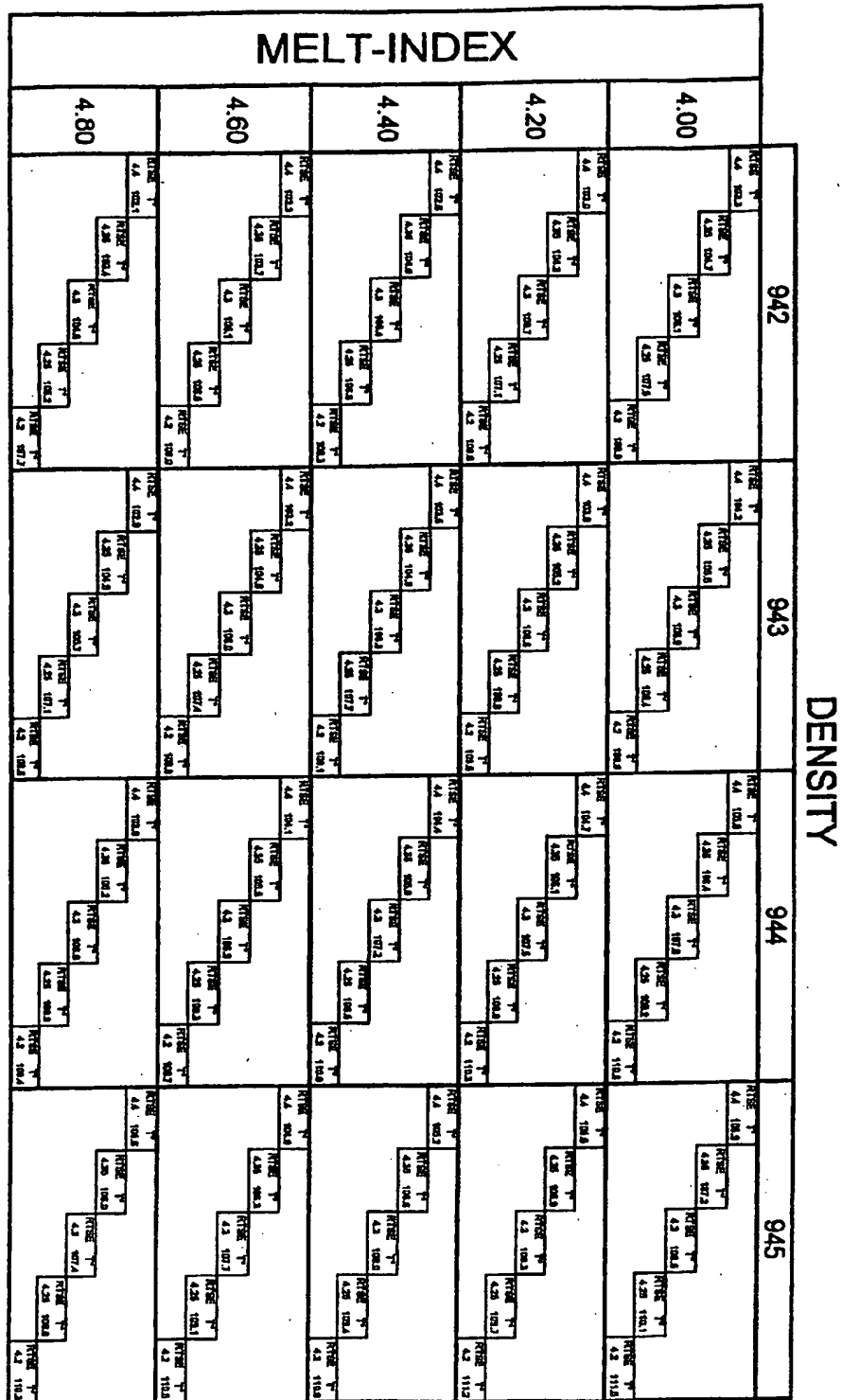


Figure 17

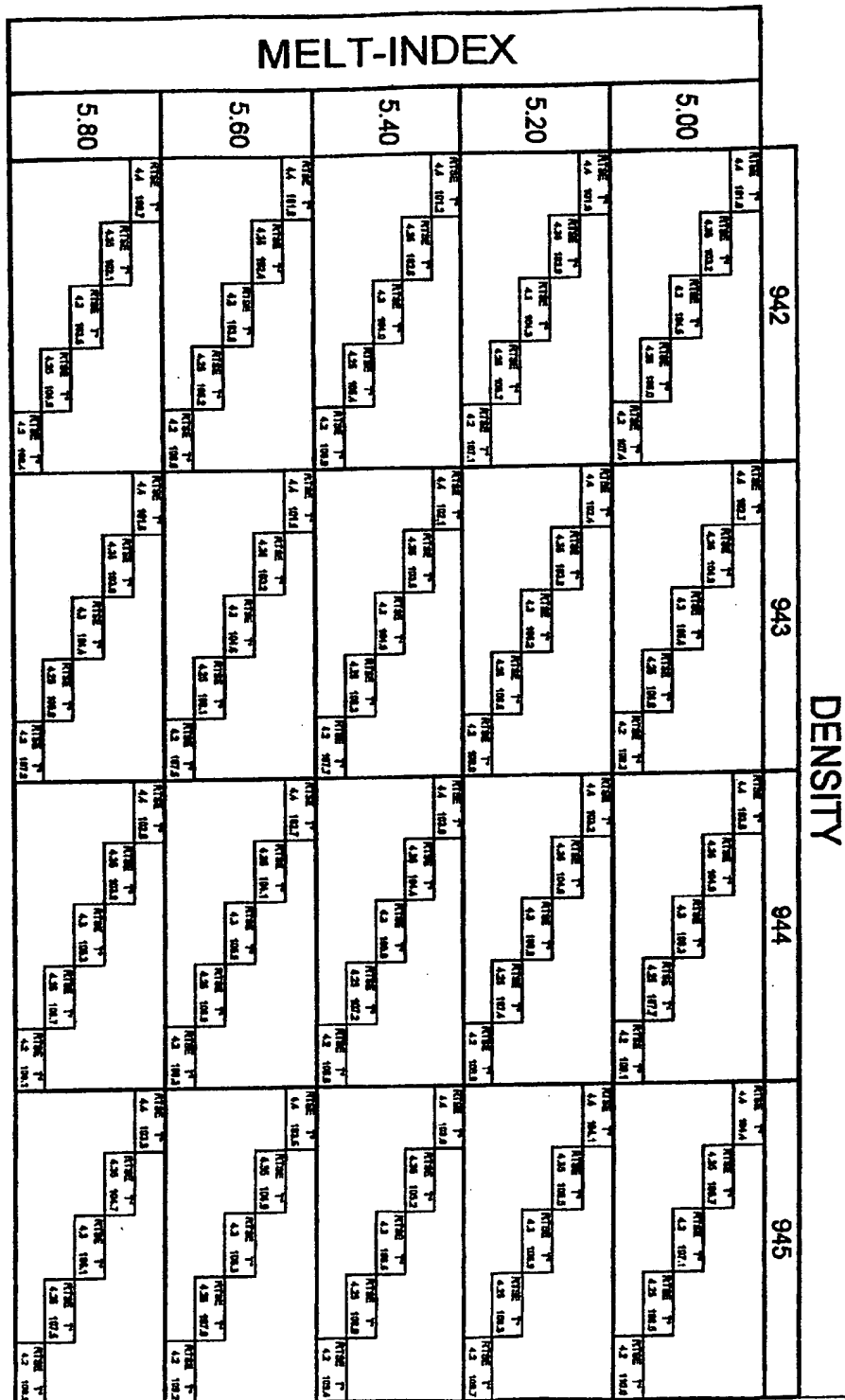


Figure 18

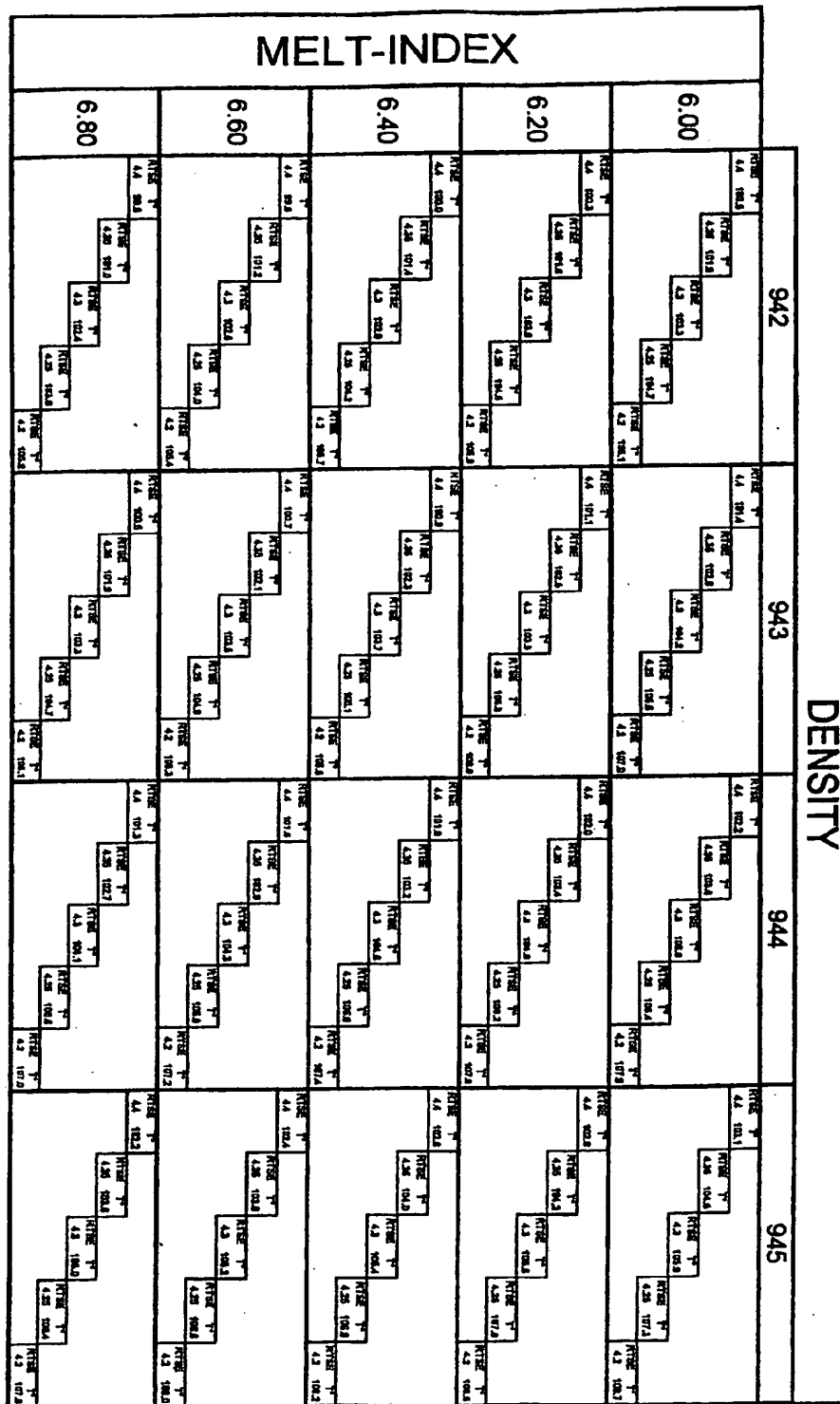


Figure 19

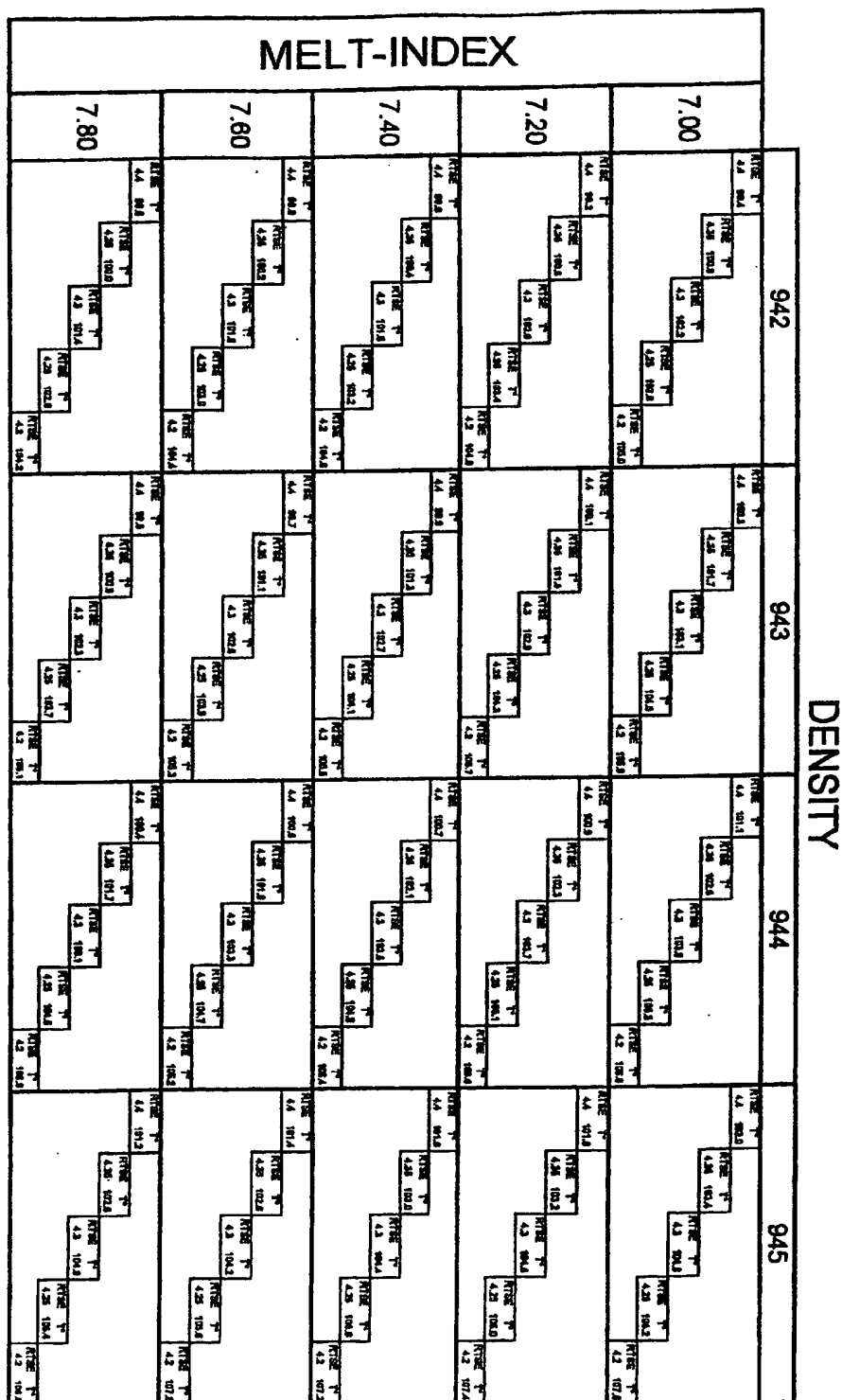


Figure 20



European Patent
Office

EUROPEAN SEARCH REPORT

Application Number
EP 02 35 8009

DOCUMENTS CONSIDERED TO BE RELEVANT			
Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (Int.Cl.7)
X	US 6 144 897 A (SELLIERS JACQUES DE) 7 November 2000 (2000-11-07) * column 11, line 8 - line 13; claims 1,9; examples *	1-10	C08F10/02 C08F2/00
Y	WO 01 49751 A (PIRAGUACY DEMORO ESDRAS ;DUARTE BRAGANCA ANTONIO LUIZ (BR); MARTIN) 12 July 2001 (2001-07-12) * claims 1,6,8,13,15,16 *	1-9	
X	US 5 530 055 A (NEEDHAM DONALD G) 25 June 1996 (1996-06-25) * claims *	10 1-9	
X	US 5 922 778 A (STREBEL JEFFREY J) 13 July 1999 (1999-07-13) * column 6, line 44 - line 49; claims *	10 1-9	
E	EP 1 236 770 A (BOREALIS TECH OY) 4 September 2002 (2002-09-04) * page 3, line 24 - line 46; claims *	1-10	
X	EP 1 172 381 A (JAPAN POLYOLEFINS CO LTD) 16 January 2002 (2002-01-16) * claims; examples *	10	
X	WO 00 69919 A (ELENAC GMBH ;EVERTZ KASPAR (DE); PERNER THOMAS (DE); DECKERS ANDRE) 23 November 2000 (2000-11-23) * claims; examples; tables *	10	
X	EP 1 041 085 A (JAPAN POLYOLEFINS CO LTD) 4 October 2000 (2000-10-04) * claims; example 16 *	10	
A	EP 0 905 145 A (FINA RESEARCH) 31 March 1999 (1999-03-31) * claims *	10	
The present search report has been drawn up for all claims			
Place of search THE HAGUE		Date of completion of the search 9 October 2002	Examiner Kaumann, E
<p>CATEGORY OF CITED DOCUMENTS</p> <p>X : particularly relevant if taken alone Y : particularly relevant if combined with another document of the same category A : technological background O : non-written disclosure P : intermediate document</p> <p>T : theory or principle underlying the invention E : earlier patent document, but published on, or after the filing date D : document cited in the application L : document cited for other reasons & : member of the same patent family, corresponding document</p>			

EPO FORM 1503 03.02 (P04C01)

**ANNEX TO THE EUROPEAN SEARCH REPORT
ON EUROPEAN PATENT APPLICATION NO.**

EP 02 35 8009

This annex lists the patent family members relating to the patent documents cited in the above-mentioned European search report. The members are as contained in the European Patent Office EDP file on
The European Patent Office is in no way liable for these particulars which are merely given for the purpose of information.

09-10-2002

Patent document cited in search report		Publication date		Patent family member(s)	Publication date
US 6144897	A	07-11-2000	BE	1009406 A3	04-03-1997
			AT	177761 T	15-04-1999
			AU	704563 B2	29-04-1999
			AU	6124696 A	09-01-1997
			BR	9609240 A	11-05-1999
			CA	2220316 A1	27-12-1996
			CN	1192222 A	02-09-1998
			CZ	9703985 A3	18-03-1998
			DE	69601794 D1	22-04-1999
			DE	69601794 T2	07-10-1999
			WO	9641822 A1	27-12-1996
			EP	0830394 A1	25-03-1998
			ES	2131945 T3	01-08-1999
			HU	9803021 A2	28-04-1999
			JP	2000500060 T	11-01-2000
			NO	975780 A	06-02-1998
			PL	323911 A1	27-04-1998
WO 0149751	A	12-07-2001	BR	9906022 A	25-09-2001
			WO	0149751 A1	12-07-2001
US 5530055	A	25-06-1996	CA	2163138 A1	10-06-1996
US 5922778	A	13-07-1999	US	5783611 A	21-07-1998
			US	6083434 A	04-07-2000
			US	5830392 A	03-11-1998
EP 1236770	A	04-09-2002	EP	1236770 A1	04-09-2002
			WO	02070602 A2	12-09-2002
EP 1172381	A	16-01-2002	EP	1172381 A1	16-01-2002
			JP	2002080521 A	19-03-2002
			US	2002042482 A1	11-04-2002
WO 0069919	A	23-11-2000	DE	19922677 C1	19-04-2001
			AU	4920600 A	05-12-2000
			CN	1350550 T	22-05-2002
			WO	0069919 A1	23-11-2000
			EP	1187855 A1	20-03-2002
EP 1041085	A	04-10-2000	JP	2001192408 A	17-07-2001
			JP	2000344820 A	12-12-2000
			DE	60000318 D1	19-09-2002
			EP	1041085 A1	04-10-2000
EP 0905145	A	31-03-1999	EP	0905145 A1	31-03-1999

EPO FORM P4489

For more details about this annex : see Official Journal of the European Patent Office, No. 12/82

ANNEX TO THE EUROPEAN SEARCH REPORT
ON EUROPEAN PATENT APPLICATION NO.

EP 02 35 8009

This annex lists the patent family members relating to the patent documents cited in the above-mentioned European search report.
The members are as contained in the European Patent Office EDP file on
The European Patent Office is in no way liable for these particulars which are merely given for the purpose of information.

09-10-2002

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
EP 0905145 A	EP	0905146 A1	31-03-1999
	JP	11189602 A	13-07-1999
	US	6252017 B1	26-06-2001
<hr/>			

EPO FORM P0459

For more details about this annex : see Official Journal of the European Patent Office, No. 12/82

THIS PAGE BLANK (USPTO)

**This Page is Inserted by IFW Indexing and Scanning
Operations and is not part of the Official Record**

BEST AVAILABLE IMAGES

Defective images within this document are accurate representations of the original documents submitted by the applicant.

Defects in the images include but are not limited to the items checked:

☐ **BLACK BORDERS**

☐ **IMAGE CUT OFF AT TOP, BOTTOM OR SIDES**

☒ **FADED TEXT OR DRAWING**

☒ **BLURRED OR ILLEGIBLE TEXT OR DRAWING**

☐ **SKEWED/SLANTED IMAGES**

☐ **COLOR OR BLACK AND WHITE PHOTOGRAPHS**

☐ **GRAY SCALE DOCUMENTS**

☐ **LINES OR MARKS ON ORIGINAL DOCUMENT**

☐ **REFERENCE(S) OR EXHIBIT(S) SUBMITTED ARE POOR QUALITY**

☐ **OTHER:** _____

IMAGES ARE BEST AVAILABLE COPY.

As rescanning these documents will not correct the image problems checked, please do not report these problems to the IFW Image Problem Mailbox.

THIS PAGE BLANK (USPTO)